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(54) **Process for the gas-phase polymerization of alpha-olefins.**

(57) The present invention relates to a process for the production of polymers and copolymers of olefins  $\text{CH}_2=\text{CHR}$ , wherein R is a hydrogen atom or an alkyl or aryl radical having a number of carbon atoms of from 1 to 10, comprising at least one (co)polymerization step in the gas phase, in the presence of a highly active catalyst obtained from a titanium compound supported on a magnesium halide in active form and an Al-alkyl compound. The process is characterized by the fact that it is carried out by feeding a small amount compared with the polymer of a compound having at least two groups, same or different, capable of reacting with the alkyl aluminum compound and able to selectively inhibit the reactivity of the polymer particles fine compared to the average granulometric size of the polymer present in the gas phase.

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The present invention relates to a process for the production of polymers and copolymers of olefins  $\text{CH}_2=\text{CHR}$ , wherein R is a hydrogen atom or an alkyl or aryl radical having a number of carbon atoms of from 1 to 10, comprising at least one (co)polymerization step in the gas phase, in the presence of a highly active catalyst obtained from a titanium compound supported on a magnesium halide in active form and an Al-alkyl compound. The process is characterized by the fact that it is carried out by adding a small amount compared with the polymer of a compound having at least two groups, same or different, capable of reacting with the alkyl aluminum compound and able to selectively inhibit the reactivity of the polymer particle fines compared with the average granulometric size of the polymer present in the gas phase.

Processes for the polymerization of one or more olefins are known which are carried out in the gas phase in fluidized or mechanically stirred bed reactors, in the presence of catalysts obtained from compounds of transition metals belonging to groups IV, V or VI of the Periodic Table of the Elements and aluminum alkyl compounds or in the presence of catalysts based on chromium oxide.

The polymer is obtained in the form of granules having a more or less regular morphology depending on the morphology of the catalyst; the dimensions of the granules depend on the dimensions of the catalyst particles and on reaction conditions and are generally distributed around an average value.

In these types of processes the heat of reaction is removed by means of a heat exchanger placed inside the reactor or in the recycle line of the reaction gas.

A generally encountered problem in polymerization processes of this type results from the presence of very fine polymer particles which are either produced from already existing fine catalyst particles or derive as a result of breakage of the catalyst itself.

These fine particles tend to deposit onto and electrostatically adhere to the inner walls of the reactor and the heat exchanger, and to thereafter grow in size by chemical reaction thus causing an insulating effect and a lower heat transfer resulting in the formation of hot spots in the reactor.

These effects are enhanced when the gas-phase alpha-olefin polymerization process is carried out in the presence of highly active catalysts such as those comprising the reaction product of an aluminum alkyl with a titanium compound supported on a magnesium halide in active form.

As a consequence a loss in fluidization efficiency and homogeneity generally occurs; for example catalyst feeding interruption may occur as well as clogging of the polymer discharge system; furthermore, excess temperature can result in particle melting with the formation of layers of thin agglomerates which adhere to the reactor walls and in the formation of agglomerates which may clog the gas distribution plate.

These drawbacks lead to poor process reproducibility and can lead to a forced interruption of the run in order to remove deposits which have formed inside the reactor even after relatively short times.

Several solutions have been proposed to avoid these drawbacks, either by acting on the catalyst activity or by reducing or eliminating the electrostatic voltage.

Patent Application EP-359444 describes the introduction into the polymerization reactor of small amounts (generally smaller than 0.1 ppm with respect to the polymerization mixture) of a retarder selected from polymerization inhibitors or substances able to poison the catalyst, in order to reduce the olefin polymerization rate. However, as described in the same patent application, the use of larger quantities of the retarder adversely affects both the quality and properties of the polymer produced, such as the melt index, the melt flow ratio and/or the stereoregularity of the polymer, as well as reducing the efficiency of the process.

U.S. Patent 4,739,015 describes the use of oxygen containing gaseous products and liquid or solid compounds containing active hydrogens to prevent the formation of agglomerates and reactor fouling in processes for preparing heterophasic propylene polymers. Among the compounds containing active hydrogens ethanol, methanol, ethylene glycol, propylene glycol and diethylene glycol are cited.

These compounds, which knowingly are polymerization inhibitors, must be used in an amount of a few ppm with respect to the polymer in order not to deactivate the catalyst; at such concentrations they are not effective as to a selective deactivation of the fine catalyst particles, whereas at higher concentrations the polymerization does not take place. Therefore, the use of the components described in said patent does not solve the problem of inhibiting the reactivity of the fine polymer particles and their consequent adhesion and fouling of the reactor walls.

Different techniques have been proposed to reduce or eliminate the electrostatic voltage responsible for the phenomena of migration and formation of deposits on the walls.

In U.S. Patent 4,803,251 a group of chemical additives is described which generate both positive and negative charges in the reactor, and which are fed to the reactor in an amount of a few ppm per part of the monomer in order to prevent the formation of undesired positive or negative charges. Also in this case the remedy may involve a deterioration in polymer quality as well as a decrease in reactor productivity.

Patent EP-B-232701 describes the use of antistatic agents to prevent the formation of crusts inside the reactor during processes for the preparation of ultra high molecular weight polyethylene (UHMWPE) wherein

the polymer is in the form of a powder having an average particle diameter smaller than 1 mm and wherein the antistatic agent is used to solve the problems associated with the presence of electrostatic charges in the ultra high molecular weight polyethylene powders. The preferred antistatic agent is a mixture of a chromium organic salt with a calcium organic salt and a phenolic stabilizer which has to be used in an amount lower than 200 ppm, preferably comprised between 5 and 100 ppm, in order not to interfere with the catalyst activity.

The antistatic agent prevents the formation of crusts inside the reactor but, as clearly shown in subsequent patents EP-A-362629 and EP-A-364759, the polymers have a rather low bulk density and in the films obtained therefrom impurities are present in the form of unmelted products.

These last patents suggest a pretreatment of the catalyst with the antistatic agent, in order to eliminate these drawbacks. To this purpose the antistatic agent, used in an amount of a few ppm by weight with respect to the final polymer but which may reach up to 1,000% by weight with respect to the catalyst, must not contain functional groups capable of deactivating the catalyst. Also by this route a certain amount of impurities still remains in the films obtained from these polymers.

Patent EP-B-229368 describes the use of antistatic agents to prevent the formation of crusts inside the reactor during polymerization or copolymerization processes of ethylene in the gas phase.

The preferred antistatic agent is a mixture of a chromium organic salt with a calcium organic salt and a phenol stabilizer which has to be used in an amount lower than 100 ppm relative to the polymer in order not to interfere with the catalyst activity.

Other processes for reducing or eliminating the electrostatic voltage include (1) installation of grounding devices in a fluidized bed, (2) ionization of gas or particles by electrical discharge to generate ions which neutralize electrostatic charges on the particles and (3) the use of radioactive sources to produce radiation capable of generating ions which neutralize electrostatic charges on the particles.

However, the use of these techniques in an industrial scale fluid bed polymerization reactor is generally neither practical or easy.

Fluidized or stirred beds consist of polymer particles having a defined geometric shape and a granulometric distribution preferably narrow and generally distributed over values higher than 500  $\mu\text{m}$ .

The presence of a significant amount of fine particles mainly deriving from breakage of a portion of the catalyst gives rise to the problem of the adhesion of these particles to the reactor walls.

None of the techniques proposed to date for preventing adhesion of the polymer to the reactor walls during gas-phase olefin polymerization processes in fluid bed systems provides a solution to the problem of inhibiting the reactivity of the fine polymer particles, which problem is to be considered among the main causes responsible for the adhesion phenomenon and for the drawbacks deriving therefrom.

Therefore, the need is felt for solutions which do not decrease the activity of the catalyst system, as it conversely occurs by using chemical compounds inhibiting polymerization reactions, and which at the same time inhibit the polymerization of fine particles which generally leads to the formation of rubbery low polymers.

It has now been surprisingly found that by using particular organic compounds in appropriate amounts it is possible to selectively deactivate the fine catalyst particles (already pre-existing or formed during polymerization) without reducing the polymerization yield or slowing down the course of the process.

By this manner fouling of the reactor walls and/or clogging of charge and discharge pipes of the reactor is avoided, while preserving at the same time process efficiency and product quality.

Differently from the additives generally used in the prior art which must be used at very low concentrations in order not to poison the catalyst, the compounds of the process of the invention are used in sufficiently large quantities so that they may concentrate on the finest catalyst particles and deactivate them.

The process of the present invention for the production of (co)polymers of olefins  $\text{CH}_2=\text{CHR}$ , wherein R is a hydrogen atom or an alkyl or aryl radical having a number of carbon atoms of from 1 to 10; comprises at least one (co)polymerization step in the gas phase in which a fluidized or stirred bed is maintained, in the presence of a catalyst comprising the product of the reaction of (1) a solid catalyst component comprising a titanium compound supported on a magnesium dihalide in active form optionally comprising an electron donor and (2) an alkyl aluminum compound optionally in the presence of an electron donor, wherein:

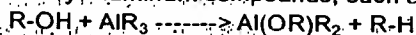
- the fluidized or stirred bed comprises granular polymer particles at least the 80% of which being larger than 500  $\mu\text{m}$  and less than 10% being smaller than 200  $\mu\text{m}$ ; and
- a compound (3), having a chain of at least 4 carbon atoms and containing at least two groups capable of reacting with the alkyl aluminum compound, is fed at any stage of the process in an amount greater than 100 ppm by weight with respect to the polymer produced, the molar ratio of the compound (3) to the alkyl aluminum compound being lower than 1;

said compound (3) being further able, when used in a standard polymerization test of mixtures of ethylene and propylene, to selectively inhibit the polymerization on polymer particles smaller than 850  $\mu\text{m}$ .

The standard test used as the evaluation criterion is described hereinbelow.

Preferably an alkane having from 3 to 5 carbon atoms is present in the gas phase during polymerization, said alkane being present in an amount of from 20 to 90% with respect to the total gas.

As groups capable of reacting with the alkyl aluminum compound such groups are intended which are able to give substitution reactions with the alkyl aluminum compounds, such as for instance the reaction



Surprisingly and unexpectedly it has been found that compounds (3) preferably concentrate on the particles having a smaller size. Owing to the reactive groups present, the alkyl aluminum compound is deactivated by reacting with said reactive groups.

The same effect is not observed with compounds which, though containing two or more reactive groups, have less than four carbon atoms in the chain, such as for instance glycerol or propylene glycol. At low concentrations said compounds do not inhibit the polymerization on the finest particles, whereas at the concentrations at which the compounds of the invention operate, they deactivate the catalyst thus not allowing the polymerization to actually take place.

Examples of compounds (3) usable in the process of the invention are:

- a) polyalcohols containing chains having, at least 4 carbon atoms, preferably from 4 to 8 carbon atoms and among these preferably sorbitol and 1,4-butanediol;
- b) hydroxyesters, having at least two free hydroxyl groups, obtained from carboxylic acids having at least 4 and preferably from 8 to 22 carbon atoms and from polyalcohols, and among these preferably glycerol monostearate and sorbitan monooleate;
- c) N-alkyl diethanolamines of formula  $CH_3(CH_2)_nCH_2-N(CH_2CH_2OH)_2$ , wherein n is greater than 2 and preferably comprised between 6 and 20. A representative compound is a commercial product sold under the trademark of Atmer 163 by ICI.
- d) polyepoxidate oils such as epoxidate linseed oil and epoxidate soya oil. Representative compounds are products sold under the trademarks Edenol D82 and Edenol B316 by Henkel.

As already specified, these compounds are fed in an amount such that their content by weight with respect to the polymer is generally comprised between 100 and 2,000 ppm, preferably between 100 and 800, and their molar ratio to the alkyl aluminum compound (2) is lower than 1 and generally comprised between 0.05 and 0.8.

The amount of compound (3) to be used varies within this range depending on the granulometric distribution of the catalyst (or of the polymer which is being formed; in the case, for instance, of the sequential polymerization of propylene and of mixtures of propylene with ethylene, wherein a homopolymerization step of propylene is followed by one or more copolymerization steps in the gas phase). Generally, larger quantities of compound (3) are used when a higher content of fine particles is present.

The quantity of compound (3) also depends on the nature itself of the compound; it has been observed for instance that compounds of class (d) generally work at lower concentrations than other compounds, all conditions being equal.

As previously indicated, the gas phase may contain an inert  $C_3-C_5$  alkane in an amount of from 20 to 90% molar, preferably from 30 to 90% molar, with respect to the total gas. Suitable alkanes include propane, butane, isobutane, n-pentane, isopentane, cyclopropane, and cyclobutane. Preferably the alkane is propane.

The alkane is fed into the reactor either with the monomer or separately and is recycled with the recycle gas, i.e., the gas stream which does not react in the bed and which is removed from the polymerization zone, preferably by passing it into a velocity reduction zone above the bed where entrained particles are given an opportunity to drop back into the bed. The recycle gas is compressed and thereafter passed through a heat exchanger before it is returned to the bed. See, for instance, U.S. Patents 3,298,792 and 4,518,750 for a description of gas-phase reactors and techniques.

The process of the present invention can be applied to the preparation of a large number of olefin polymers without the previously described drawbacks being observed. Examples of polymers which can be obtained are:

- high density polyethylenes (HDPE, having a density greater than  $0.940 \text{ g/cm}^3$ ), including homopolymers of ethylene and copolymers of ethylene with alpha-olefins having from 3 to 12 carbon atoms;
- linear low density polyethylenes (LLDPE, having a density lower than  $0.940 \text{ g/cm}^3$ ) and very low and ultra low density linear polyethylenes (VLDPE and ULDPE, having a density lower than  $0.920 \text{ g/cm}^3$  and as low as  $0.880 \text{ g/cm}^3$ ) consisting of copolymers of ethylene with one or more alpha-olefins having from 3 to 12 carbon atoms;
- elastomeric terpolymers of ethylene and propylene with minor amounts of a diene, and elastomeric copolymers of ethylene and propylene having a content of units derived from ethylene comprised between about 30 and 70% by weight; isotactic polypropylenes and crystalline copolymers of propylene and ethylene and/or other alpha-olefins having a content of units derived from propylene of over 85% by weight;

impact polymers of propylene obtained by sequential polymerization of propylene and of propylene-ethylene mixtures containing up to 30% by weight of ethylene.

The process of the invention is particularly advantageous for the production of LLDPE, VLDPE, ULDPE, heterophasic propylene copolymers and elastomeric copolymers of ethylene with propylene and optionally minor amounts of a diene. In fact, in these cases the problem of reactor fouling and clogging of charge and discharge pipes of the reactor because of the presence of fine rubbery particles is particularly exacerbated without this invention.

In polymers obtained according to the process of the invention, it is observed that compound (3) is selectively concentrated on the fraction of the polymer having a smaller size.

Compound (3) may be fed at any stage of the polymerization process.

An example of the process of the invention is represented in the enclosed Figure 1, which is used for the production of heterophasic propylene copolymers: The plant comprises a loop reactor R1 which polymerizes propylene in the liquid phase to homopolymer and two gas-phase reactors in series R2 and R3, wherein the copolymerization of the gaseous ethylene-propylene mixture to a rubbery copolymer takes place, the rubbery copolymer growing onto the homopolymer matrix coming from the loop. Into the loop reactor R1 are fed (through line 1) the liquid propylene, the different catalyst components and optionally hydrogen as molecular weight regulator. The polymer suspension exiting the loop is allowed to enter a flash tube lined and heated with vapor, within which evaporation of the unreacted propylene takes place. To this tube component (3) is fed through line 2 in order to inhibit the subsequent formation of rubbery copolymers onto the fine particles of the homopolymer. In the cyclone D1 the gaseous propylene (which is recycled after liquefaction in E3, to the loop reactor R1) is separated from the homopolymer which is fed to the reactor R2 through line 3. Line 4 represents the feeding of the ethylene/propylene mixture and optionally hydrogen, through the recycle lines, to reactors R2 and R3. Thermoregulation of reactor R2 and R3 is performed by recycling the reactants through the exchangers E1 and E2 and compressors P1 and P2. The copolymerization takes place in the two reactors R1 and R2 and the final polymer produced is discharged through line 5.

Another example of plant flow sheet usable for the process of the present invention is represented in Figure 2. The plant comprises a reactor R1 wherein small amounts of monomer are prepolymerized in the presence of the catalyst components and two fluid bed reactors, R2 and R3, wherein the gas-phase polymerization takes place. Using said plant, component (3) is added after the prepolymerization step, before introducing the prepolymer into the first gas-phase reactor R2; optionally and advantageously component (3) can be partially added even after the first gas-phase reactor R2, before the optional introduction of the polymer being formed into the second gas-phase reactor R3.

The catalyst used in the process of the invention comprises the reaction product of:

1) a solid component comprising a titanium compound supported on a magnesium dihalide in active form. The solid component may also comprise an electron donor compound (inside donor). Generally the inside donor is always used when the solid component is employed to prepare catalysts for the stereoregular polymerization of propylene, butene-1 and similar  $\alpha$ -olefins in which a high stereospecificity is needed to obtain polymers exhibiting an Isotacticity Index higher than 90, preferably higher than 95.

2) an alkyl aluminum compound, optionally in the presence of an electron donor compound (outside donor). When the process of the invention is used to produce stereoregular polymers, for instance propylene polymers having a high Isotacticity Index, the outside donor is used to impart the catalyst the necessary high stereospecificity. However, when diethers of the type described herein after are used as the inside donor, the catalyst stereospecificity is in itself sufficiently high and no outside donor is necessary.

The active magnesium dihalide used as support of the Ziegler-Natta catalysts are extensively described in the patent literature. U.S. Patents 4,298,718 and 4,495,338 have described for the first time the use of these supports.

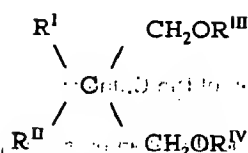
The active magnesium dihalide present as support in the catalyst component used in the process of the present invention are characterized by X-ray spectra wherein the most intense diffraction line which appears in the spectrum of the non-active halide has reduced intensity and is substituted by a halo with the maximum intensity shifted towards lower angles with respect to the angle of the most intense line.

Preferably the magnesium halide is magnesium dichloride.

The titanium compounds suitable for the preparation of the solid component include titanium halides such as  $\text{TiCl}_4$ , which is preferred,  $\text{TiCl}_3$  and titanium alcoholates such as trichlorophenoxy- and trichlorobutoxy titanium.

The titanium compound may be used in mixture with other transition metal compounds such as vanadium, zirconium and hafnium compounds.

Suitable inside electron-donors include ethers, esters, amines, ketones and diethers of the general formula



wherein  $R^I$  and  $R^{II}$ , the same or different from each other, are alkyl, cycloalkyl and aryl radicals having a number of carbon atoms of from 1 to 18 and  $R^{III}$  and  $R^{IV}$ , the same or different from each other, are alkyl radicals with a number of carbon atoms of from 1 to 4.

Preferred compounds are the alkyl, cycloalkyl and aryl esters of polycarboxylic acids such as phthalic and maleic acid and the previously described diethers wherein  $R^{III}$  and  $R^{IV}$  are  $CH_3$  groups.

Examples of said compounds are di-n-butylphthalate, di-isobutylphthalate, di-n-octylphthalate, 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2-methyl-2-isobutyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, and 2-isopropyl-2-isopentyl-1,3-dimethoxypropane.

The inside donor is generally present in a molar ratio to the Mg of from 1:8 to 1:14. The titanium compound, expressed as Ti, is generally present in an amount of from 0.5 to 10% by weight. Examples of usable solid components are described in U.S. Patents 4,474,221, 4,803,251 and 4,302,566 the preparation method of which is herein incorporated by reference.

Using the catalysts obtained from the catalyst components described in Patent EP-A-344755 the description of which is herein incorporated by reference, it is possible to prepare spherical polymers having an average diameter comprised between 300 and 5,000  $\mu m$  and in the case of ethylene and propylene, polymers having a very high bulk density.

The invention can also be applied to the preparation of polymers having a regular geometric shape different from the spherical shape. Examples of said polymers are those which can be obtained using the supports and catalysts described in patent application EP-A-449673.

Also falling within the class of components usable in the process of the invention are the compounds described in U.S. Patent 4,472,520 and 4,218,339.

The alkyl aluminum compound (2) is selected among aluminum trialkyls such as Al-triethyl, Al-triisobutyl, Al-tri-n-butyl, Al-tri-n-hexyl, Al-tri-n-octyl. Mixtures of Al-trialkyls with Al-trialkylhalides or Al-alkyl-sesquichlorides such as  $AlEt_2Cl$  and  $Al_2Et_3Cl_3$  can also be used.

The Al/Ti ratio in the catalyst is greater than 1 and it is generally comprised between 10 and 4,000, preferably between 20 and 800.

The outside donor may be the same or different from the electron-donor compound present as the inside donor. If the inside donor is an ester of a polycarboxylic acid, in particular a phthalate, the outside donor is preferably selected among silicon compounds of the formula  $R_1R_2Si(OR)_2$  wherein  $R_1$  and  $R_2$  are alkyl, cycloalkyl or aryl radicals having from 1 to 18 carbon atoms. Examples of these silanes are methyl-cyclohexyl-dimethoxy-silane, diphenyl-dimethoxy-silane, and methyl-t-butyl-dimethoxy-silane.

The efficiency of the process of the invention has been evaluated by some standard tests aimed at evaluating the performance of some compounds as selective inhibitors in regard to very fine particles.

The method used consists of a two-step polymerization carried out in the same autoclave; in the first step polymerization to propylene homopolymer is carried out, in liquid propylene, and in the second step, after degassing, a gas-phase copolymerization onto the homopolymer matrix is carried out using a gaseous mixture of ethylene and propylene. Before degassing a certain quantity of the chemical compound (3) is added to the autoclave.

The ability to reduce the formation of rubbery copolymers is evaluated through the content of ethylene respectively bound onto the granulometric fractions having a diameter greater than 850  $\mu m$  and onto the fractions having a diameter smaller than 850  $\mu m$ .

If the ethylene content in the fraction <850  $\mu m$  is significantly lower than the content in the fraction >850  $\mu m$  (ratio of the content in the fraction >850  $\mu m$  to the content in the fraction <850  $\mu m$  equal to or greater than 1.15) compound (3) is considered to be an effective inhibitor and it can therefore be used in the process of the invention.

The effectiveness is also evaluated in terms of the polymerization yield, in that the yield has to be at the same level as in the test carried out in the absence of compound (3).

From the process of the invention, without any drawback during the synthesis step and with high yields, polyolefins are obtained wherein compound (3) is concentrated onto the polymer particles having a smaller size.

The following examples can further illustrate the present invention and have not to be intended as limitative



of the invention itself.

#### General Procedure for the Preparation of the Catalyst

5 The catalyst component (1) used in the examples was prepared as follows.

Under an inert atmosphere, 28.4 g of  $MgCl_2$ , 49.5 g of anhydrous ethanol, 10 ml of ROL OB/30 vaseline oil, and 100 ml of silicone oil having a viscosity of 350 cs were introduced into a reaction vessel equipped with a stirrer and heated at 120°C until the  $MgCl_2$  was dissolved. The hot reaction mixture was then transferred to a 1,500 ml vessel equipped with an Ultra Turrax T-45 N stirrer and containing 150 ml of vaseline oil and 150  
10 ml of silicone oil. The temperature was maintained at 120°C while stirring for 3 minutes at 3,000 rpm. The mixture was then discharged into a 2 liter vessel equipped with a stirrer and containing 1,000 ml of anhydrous n-heptane cooled at 0°C. The obtained particles were recovered by filtering, washed with 500 ml aliquots of n-hexane and heated gradually by increasing the temperature from 50°C to 100°C for a period of time sufficient to reduce the alcohol content from 3 mole to the contents indicated in the various examples.

15 25 g of the adduct, containing the various quantities of alcohol specified in the examples, were transferred into a reaction vessel equipped with a stirrer and containing 625 ml of  $TiCl_4$  at 0°C under agitation, and thereafter the temperature was raised to 100°C in one hour, when the temperature reached 40°C, diisobutylphthalate was added in an amount such that the molar ratio of magnesium to the phthalate was 8.

The contents of the reactor vessel were then heated at 100°C for two hours, under agitation, then the agitation was stopped and the solid was allowed to settle.

The hot liquid was removed by siphon. 500 ml of  $TiCl_4$  were added and the mixture was heated at 120°C for one hour under agitation. The agitation was interrupted and the solid was allowed to settle. The hot liquid was removed by siphon. The solid was washed with aliquots of n-hexane at 60°C and thereafter at room temperature.

#### 25 EXAMPLES 1-7

The following examples relate to some standard tests aimed at evaluating the effectiveness of some compounds as inhibitors of fine particles in the process of the invention and are concerned with the preparation  
30 of heterophasic propylene copolymers.

The tests were carried out in a 4 liter autoclave for polymerization tests. After degassing and washing with propylene the autoclave was kept at 30°C under a moderate propylene flow.

The run was carried out by feeding a catalyst complex dispersed in hexane and comprising 0.01 g of a solid catalyst component prepared according to the previously described general procedures using a  $MgCl_2$ -ethanol adduct containing 50% by weight of alcohol, 0.76 g of aluminum triethyl (TEAL) and 0.081 g of diphenyldimethoxy-silane as the outside donor. Thereafter a quantity of hydrogen was fed to obtain a Melt Index 'I' within the range of values of from 2 to 6; agitation continued while feeding propylene in an amount of 2.3 litres at normal temperature.

The temperature was raised to 70°C and the polymerization to propylene homopolymer was carried out  
40 for 110 minutes. The temperature was lowered by 10°C and compound (3) was injected dissolved in 20 cc of hexane, polymerizing thereafter for an additional 10 minutes.

At this point the agitation was stopped and the propylene was degassed to 5 bar while keeping the temperature constant at 70°C. The polymerization was resumed by feeding ethylene up to a total of 10 bar and maintaining the pressure by feeding a preformed ethylene/propylene mixture in a 65/35 molar ratio. Said mixture was fed up to 15% by weight of the final product. Finally degassing was carried out to end.

45 In Table 1, besides the operating conditions of the copolymerization step, the contents of bound ethylene on the granulometric fraction having diameter larger than 850  $\mu m$  and on the fraction having diameter smaller than 850  $\mu m$  respectively are reported.

#### 50 COMPARATIVE EXAMPLE 8

A heterophasic propylene copolymer was prepared according to the operating method described in Examples 1-7, but without adding any compound before the copolymerization step. The results in Table 1 clearly show that the ethylene content is substantially the same both on the fractions having a granulometry > 850  
55  $\mu m$  and on those having a granulometry < 850  $\mu m$ .

COMPARATIVE EXAMPLE 9

A heterophasic propylene copolymer was prepared according to the procedures described in Examples 1-7, but using as the inhibitor agent a compound which does not contain functional groups. An M100 silicon oil was used in an amount equal to 0.76 g. This compound, for a mole ratio of 0.126 to TEAL, was found to affect the reaction rate, but did not cause a reduction in the amount of bound ethylene on the fine fractions.

COMPARATIVE EXAMPLES 10a, 10b, 11

Comparative Example 9 was repeated using as inhibitors difunctional or polyfunctional compounds containing less than 4 carbon atoms. Monopropylene glycol and glycerol were used in the amounts indicated in Table 1. The results reported in Table 1 show that low percentages of monopropylene glycol (propylene glycol/TEAL = 1.5 molar) are not effective (Example 10a); a higher percentage (propylene glycol/TEAL = 2.24 molar) is effective but it significantly slows the reaction (Example 10b); glycerol is not effective (Example 11).

EXAMPLE 12

A polymerization test to heterophasic copolymer has been carried out in a pilot plant to verify the anti-fouling effect of a compound selected according to the tests described in Examples 1-11.

The plant is described in Figure 1 and as the inhibitor compound Atmer 163 was used. Liquid propylene at a flow rate of 90 kg/hr, the catalyst prepared according to the previously described general procedures using a  $\text{MgCl}_2$ -ethanol adduct containing 45% by weight of alcohol, TEAL in an amount of 0.32 g/kg propylene, the outside donor In a weight ratio TEAL/donor = 3, hydrogen as molecular weight regulator in an amount of 0.02 kg/kg propylene (feed line 1) were fed to the loop reactor R1.

The polymer suspension exiting the loop was allowed to pass through a flash tube lined and heated with vapor, wherein evaporation of the unreacted propylene took place. To this tube, through line 2, Atmer 163 (60 kg/hr) was fed. After passing through the cyclone D1 the polymer was fed to the first fluid bed reactor R2 at a rate equal to 21 kg/hr (line 3). The ethylene and propylene gaseous mixture fed through line 4 to produce the copolymer in the gas phase contained 38% ethylene; hydrogen was also present in a mole ratio  $\text{H}_2/\text{C}_2 = 0.014$ . The polymerization took place in the two reactors in series and the final polymer was produced in an amount equal to 43 kg/hr.

The polymerization conditions in the loop reactor were:

Temperature 70°C

Pressure 30 bar

Residence time 105 min.

The polymerization conditions in the gas-phase reactors were:

	1st Reactor	2nd Reactor
Temperature	70°C	60°C
Pressure	12 bar	7 bar
Residence time	62 min	54 min.

The cyclone for the propylene/polymer separation between the loop and the gas-phase reactor was kept at 70°C and 14 bar.

The final characteristics of the polymer produced are: Melt Index 'L' = 0.69 g/10 min; poured bulk density = 0.42 g/cc.

In order to verify the effectiveness of Atmer 163 a sample having a total ethylene content with respect to the polymer equal to 27.5% by weight has been taken after a 4 day running period; the ethylene content on the fractions having a granulometry larger than 710  $\mu\text{m}$  was equal to 31.3%, whereas the content on the fractions having a granulometry smaller than 710  $\mu\text{m}$  was equal to 18.7%. The quantity of Atmer 163 determined by nitrogen analysis on the large fractions (>710  $\mu\text{m}$ ) was 580 ppm, whereas on the fine fractions (<710  $\mu\text{m}$ ) it was 4,060 ppm.

The plant ran for a total of 6 days with the same set-up and the same type of product without any fouling problem in the reactor or in any other process apparatus.

The same test, carried out under the same conditions but without the Atmer being present, has been interrupted after about 1 day in that clogging of the gas distribution grid and the polymer discharge pipes occurred.

### EXAMPLE 13

A pilot plant operating in continuous for the preparation of LLDPE is used. The plant, illustrated in Figure 2, comprises a prepolymerization reactor R1, to which were fed a solid catalyst component prepared according to the previously indicated general procedures using  $MgCl_2$ -ethanol adduct containing 45% by weight of alcohol; a solution of alkyl aluminum in an inert hydrocarbon, an electron donor compound and a small amount of propylene (line 1). Downstream this section the reaction took place in two gas-phase reactors in series R2 and R3. The stream coming out from the polymerization reactor (line 3), consisting of a slurry of prepolymer (polypropylene) in an inert liquid, was contacted with a stream of Atmer 163 in a determined ratio to the aluminum alkyl (line 2) and was thereafter sent to the first gas-phase polymerization stage.

The reaction monomers fed through line 4 were as follows:

- ethylene and butene;
- hydrogen as molecular weight regulator.

The product was discharged from the second gas-phase reactor through line 5.

### Main Operating conditions

Temperature 25 °C

Residence time 87 min.

#### 1st Gas-Phase Reactor

Temperature 75 °C

Pressure 18 bar

Atmer/TEAL 0.5 (by weight)

$H_2/C_2$  0.16 (molar)

$C_4/(C_2+C_4)$  0.118 (molar)

#### 2nd Gas-Phase Reactor

Temperature 75 °C

Pressure 17 bar

$H_2/C_2$  0.213 (molar)

$C_4/(C_2+C_4)$  0.134 (molar)

### Final Characteristics of the Product

Real density 0.919 kg/l

Melt Index "E" 1.1 g/10 min.

The average polymer productivity was 75 kg/hr.

The plant ran with the same set-up and the same type of product for about 9 days under conditions of absolute reliability.

**EXAMPLE 14**

A pilot plant operating in continuous for the preparation of LLDPE was used. The plant, illustrated in Figure 2, comprised a prepolymerization reactor R1, to which were fed (line 1) a solid catalyst component prepared according to the previously indicated general procedures using  $\text{MgCl}_2$ -ethanol adduct containing 45% by weight of alcohol, a solution of alkyl aluminum in an inert hydrocarbon, an electron donor compound and a small amount of propylene. Downstream this section the reaction was carried out in two gas-phase reactors in series, R2 and R3. The stream coming out from the polymerization reactor (line 3) and consisting of a slurry of prepolymer (polypropylene) in an inert liquid, was contacted with a stream of Atmer 163 in a certain ratio to the aluminum alkyl (line 2) and was thereafter sent to the first gas-phase polymerization stage.

The reaction monomers fed through line 4 were as follows:

- ethylene and butene;
- hydrogen as molecular weight regulator.

The product was discharged from the second gas-phase reactor through line 5.

Main Operating conditions	
Prepolymerization Step R <sub>1</sub>	
Temperature	25 °C
Residence time	137 min.
1st Gas-Phase Reactor	
Temperature	70 °C
Pressure	18 bar
Atmer/TEAL	0.5 (by weight)
H <sub>2</sub> /C <sub>2</sub>	0.36 (molar)
C <sub>4</sub> /(C <sub>2</sub> +C <sub>4</sub> )	0.21 (molar)
Propane/C <sub>2</sub>	1.54 (molar)
2nd Gas-Phase Reactor	
Temperature	70 °C
Pressure	15 bar
H <sub>2</sub> /C <sub>2</sub>	0.346 (molar)
C <sub>4</sub> /(C <sub>2</sub> +C <sub>4</sub> )	0.275 (molar)
Propane/C <sub>2</sub>	0.784 (molar)
Final Characteristics of the Product	
Real density	0.909 kg/l
Melt Index "E"	2.0 g/10 min.

The average polymer productivity was 63 kg/hr.

The plant ran with the same set-up and the same type of product for about 9 days under conditions of absolute reliability.

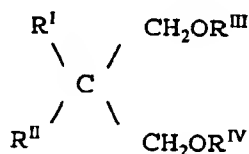
TABLE 1

Ex. No.	Compound Used (g)	COPOLYMERIZATION			% Ethylene on fraction > 850 $\mu$ m	% Ethylene on fraction < 850 $\mu$ m	Compound (3) (ppm by weight on polymer)
		Compound (3)/TEAL (mol)	Duration	Yield Kg/g. cat			
1	EDENOL D82 (0.38)	0.06	90	47.5	14.0	9.0	800
2	EDENOL B316 (0.38)	0.06	55	44.3	12.9	5.5	820
3	SORBITAN-MONOOLEATE (0.38)	0.127	65	52.6	17	7.6	720
4	GLYCEROL-MONOSTEARATE (0.38)	0.158	70	45	16	13.5	850
5	1,4-BUTANE-DIOL (0.2)	0.33	60	46	14.5	7.6	435
6	ATMER (0.76)	0.29	60	46	10.3	8.3	1650
7	SORBITOL (0.76)	0.63	50	44	13.0	6.4	1650
8 comp	TEST WITHOUT COMPOUND (3)	---	40	45.7	12.5	12.0	---
9 comp	M100 SILICON OIL (0.76)	0.126	80	47	13.1	14.0	1617
10a comp	MONOPROPYLENE GLYCOL (0.76)	1.5	50	44.2	11.0	11.5	1434
10b comp	MONOPROPYLENE GLYCOL (1.14)	2.24	90	35.8	7.0	2.2	2150
11 comp	GLYCEROL (0.55)	0.90	30	36.4	16.5	17.6	1170

## Claims

1. A process for the production of (co)polymers of olefins  $\text{CH}_2=\text{CHR}$ , wherein R is a hydrogen atom or an alkyl or aryl radical having from 1 to 10 carbon atoms, comprising at least one (co)polymerization step in the gas phase in which a fluidized or stirred bed is maintained, in the presence of a catalyst comprising the product of the reaction of (1) a solid component comprising a titanium compound supported on a magnesium dihalide in active form optionally comprising an inside electron donor and (2) an alkyl aluminum compound optionally in the presence of an outside electron donor, said process being characterized in that:

- 5
- said fluidized or stirred bed comprises granular polymer particles at least 80% of which being larger than 500  $\mu\text{m}$  and less than 10% being smaller than 200  $\mu\text{m}$ ; and
  - a compound (3), having a chain with at least 4 carbon atoms and containing at least two groups, same or different, capable of reacting with the alkyl aluminum compound (2), is fed at any stage of the process in an amount greater than 100 ppm by weight with respect to said (co)polymer, the molar ratio of the compound (3) to said alkyl aluminum compound (2) being lower than 1;
- 10
2. The process according to claim 1, characterized in that the compound (3) is selected among those belonging to one of the following classes:
- (a) polyalcohols containing chains having from 4 to 8 carbon atoms;
  - (b) hydroxyesters, having at least two free hydroxyl groups, obtained from carboxylic acids having from 8 to 22 carbon atoms and from polyalcohols;
  - 15 (c) N-alkyl-diethanolamines of formula:  $\text{CH}_3(\text{CH}_2)_n\text{CH}_2\text{-N}(\text{CH}_2\text{CH}_2\text{OH})_2$ , wherein n is greater than 2; and
  - (d) polyepoxidate unsaturated oils.
- 20
3. The process according to claim 2, characterized in that the compound (3) is selected from the group consisting of 1,4-butanediol, sorbitol, glycerol-monostearate, sorbitan-monooleate, epoxidate linseed oil, epoxidate soya oil, N-alkyl -diethanolamines of formula  $\text{CH}_3(\text{CH}_2)_n\text{CH}_2\text{-N}(\text{CH}_2\text{CH}_2\text{OH})_2$ , where n is comprised between 6 and 20.
- 25
4. The process according to claim 1, characterized in that the compound (3) is fed in an amount comprised between 100 and 2,000 ppm by weight with respect to the final polymer, the molar ratio of the compound (3) to the alkyl aluminum compound being comprised between 0.05 and 0.8.
- 30
5. The process according to claim 1, characterized in that an alkane having from 3 to 5 carbon atoms is present in the gas phase in a molar concentration of from 20 to 90% with respect to the total gas.
6. The process according to claim 5, characterized in that the alkane is propane.
- 35
7. The process according to claim 1, characterized in that the titanium compound comprises at least one halide-Ti bond.
8. The process according to claim 1, characterized in that the solid component comprises the inside electron donor and the reaction is conducted in the presence of the outside electron donor.
9. The process according to claim 1, characterized in that the inside electron donor compound is a diether having the formula:



wherein  $\text{R}^{\text{I}}$  and  $\text{R}^{\text{II}}$ , the same or different from each other, are alkyl, cycloalkyl and aryl radicals having a number of carbon atoms of from 1 to 18.

- 50
10. The process according to claim 8, characterized in that the solid component (1) has a spherical shape.
11. The process according to claim 9, characterized in that the solid component (1) has a spherical shape.
12. Products of processes according to any of claims 1 to 11.
- 55
13. Granular polymers of olefins obtained by the processes according to any of claims 1 to 9, characterized in that the compound (3) is concentrated on polymer particles smaller than 700  $\mu\text{m}$ .
14. Spherical polymers of olefins obtained by the process according to claim 10, characterized in that the

compound (3) is concentrated on polymer particles smaller than 700  $\mu\text{m}$ .

15. Ethylene (co)polymers obtained according to the process of claim 1, characterized in that the compound (3) is concentrated on polymer particles smaller than 700  $\mu\text{m}$ .

16. Propylene (co)polymers obtained according to the process of claim 8 or 9, characterized in that the compound (3) is concentrated on polymer particles smaller than 700  $\mu\text{m}$ .



European Patent  
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# EUROPEAN SEARCH REPORT

Application Number

EP 93 10 1285

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,Y	EP-A-0 359 444 (BP. CHEMICALS) * claims 1-6 * * example 1 *	1	C08F10/00 C08F2/34 C08F4/649
P,Y	EP-A-0 488 533 (UBE INDUSTRIES) * claims 1,2,4,5 * * examples 3,4 *	1	
D,A	EP-A-0 362 629 (BASF AKTIENGESELLSCHAFT) * claims 1,6 *	1	
A	EP-A-0 241 560 (SUMITOMO CHEMICAL COMPANY) * claim 2 *		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18 MAY 1993	Examiner FISCHER B.R.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  I : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

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